DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

C304 **ANALYTICAL CHEMISTRY I**

DECEMBER 2010 FINAL EXAMINATION

Time Allowed: **Three (3) Hours**

Instructions:

1. **This examination has six (6) questions and one (1) data sheet. The total number of pages is four (4), including this page.**
2. **Answer any four (4) questions fully; diagrams should be clear, large and properly labeled. Marks will be deducted for improper units and lack of procedural steps in calculations.**
3. **Each question is worth 25 marks.**

Special Requirements

1. **Data sheet.**
2. **Graph paper.**

YOU ARE NOT SUPPOSED TO OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GIVEN BY THE CHIEF INVIGILATOR.

QUESTION 1 [25]

a. Discuss each of any three (3) desirable properties of a solid support for gas chromatography, and explain how each property relates to the Van Deempter equation. [6]

b. Describe the solid support "Chromosorb W – AW - DMCS". [4]

c. Fully explain the meaning of the expression "chromatography is a semi-batch, differential migration, phase distribution technique". [6]

d. Write down the equation for Gaussian peaks in chromatography, explain all terms appearing in it, and explain the analytical significance of its integral. [5]

e. Describe each of the two ways of performing elution in Liquid Chromatography, and explain why one would prefer elution in each case. [4]

QUESTION 2 [25]

a. i) Using the Na Grotrian diagram, explain the fundamental difference between Atomic Absorption and Atomic Emission spectroscopy, and how this difference manifests itself on the optical components of the two instruments. (3)

ii) "Nebulization is a very inefficient approach to atomization". Explain the meaning and significance of this phase. (3)

ii) Explain how nebulization is bypassed altogether in GFAAS. (3)

iii) Outline the three (3) major cycles that lead to atomization in GFAAS. (3)

iv) List and describe each of three (3) advantages that GFAAS has over flame methods of atomic spectroscopy. (3)

b. What is meant by "Eddy Diffusion" in chromatography? Write down the "Eddy Diffusion" term in the Van Deempter equation, and explain how it could experimentally be manipulated to improve resolution. (4)

c. List and describe any three (3) desirable properties of a stationery phase in gas chromatography (3)

d. Describe each of the two ways of eluting compounds in gas chromatography, and explain why one would be preferred over the other. (3)

QUESTION 3 [25]

a. i) Use a diagram to explain how a band reject filter works (2)
ii) Use a diagram to explain how a cut-in/cut-off filter works (2)

b. Explain using diagrams why the sodium $^2S_{1/2} \longrightarrow {}^2P_{3/2}$ doublet consists of lines, whereas the $\pi \longrightarrow \pi^*$ of acetone appears as a band (4)

c. i) What is meant by "efficiency" of a column in liquid chromatography? (2)

ii) How does efficiency affect the height equivalent to a theoretical plate in liquid chromatography? (2)

d. i) Use diagrams to explain the effect of stationery liquid loading on resolution in gas chromatography. (4)

ii) Use diagrams to explain the effect of choice of carrier gas between He and N_2 in gas chromatography. (4)

iii) What are "silanol" groups in gas chromatography? Why are they not desired in gas chromatography? How are they masked in gas chromatography? (5)

QUESTION 4 [25]

a. In the table below,

Spectral Region	Energy (J)	Type of Transition	Wavelength (nm)	Frequency (sec^{-1})	Wavenumber (cm^{-1})	Energy (eV)
gamma rays		A		$>10^{20}$		
x-ray		B				120
uv-visible	F	C	700	H		I
infra-red		D			4,000	
micro-wave			G	10^8	J	

i. State A, B, C, D [4]

ii. Calculate F, G, H, I, J [5]

b. On a single plot, draw the blackbody radiation profiles of sources heated at 500 K and at 2000 K. [2]

c. Explain why the 500 K plot in (b) above is the ideal one for use as an IR source, and explain its implication on resolution. [2]

d. In gas chromatography, longitudinal diffusion affects resolution.

i) Use diagrams to explain what longitudinal diffusion means in gas chromatography (2)

ii) State the equation that describes the HETP term due to longitudinal diffusion in the Van Deempter equation, and explain all terms appearing in it. (3)

e. In liquid chromatography, resistance to mass transfer in the stationary phase affects resolution.

i) Use diagrams to explain what resistance to mass transfer in the stationery phase means in liquid chromatography (3)

ii) State the equation that describes the HETP term due to resistance to mass transfer in the stationery phase in the Van Deempter equation, and explain all terms appearing in it. (4)

QUESTION 5 [25]

a. State the Maxwell Boltzman equation, and explain how it is used to determine whether atomic emission or atomic absorption can be used in a measurement during trace elemental analysis. [3]

b. i). Draw a cross section of an air-acetylene flame. [3]

ii). Explain how a tear drop-shaped plasma is formed in ICP-OES, and explain why it is not analytically useful. [3]

c. With respect to the doughnut-shaped plasma in ICP-OES, given an estimate of the following operational parameters.

Temperature [1] Frequency [1] Power [1]

d. Explain how ICP reigns supreme over flame or electrothermal atomization in atomic spectroscopy in terms of linear dynamic range. [2]

e. No matter what GFAAS or ICP can offer to elemental analysis in terms of extraordinary detection limits, chromatography still remains the supreme technique for separation and subsequent detection of organic analytes in a mixture.

i). State the equation describing efficiency of a separation column in chromatography as a function of retention time and bandbroadening as solutes elute through a column. [2]

ii). State the equation describing resolution of two adjacent peaks as a function of retention time and bandbroadening as solutes elute through a column. [2]

iii). Use diagrams to explain how the detection of para- and ortho- anilines in ink is possible in HPLC using a flow through cell [4].

QUESTION 6 [25]

a. Explain why the molecule HCl is infra-red active, whereas the molecule O_2 is not (2)

b. Explain the cause of atmospheric absorption bands in infra-red spectroscopy, why they are undesirable, and how they are eliminated. (5)

c. Explain the difference in sample placement between UV-visible spectroscopy and infra-red spectroscopy (4)

d. Explain why in the determination of Zn and K in soils, emission is favored for K, whereas absorption is favored for Zn. [2]

e. With respect to Ca, explain chemical interference in flame atomic absorption spectrometry and explain how it is eliminated. [4]

f. In chromatography, resistance to mass transfer in the mobile phase affects resolution.

i. Use diagrams to explain what resistance to mass transfer in the mobile phase means in liquid chromatography (2)

ii. State the equation that describes the HETP term due to resistance to mass transfer in the mobile phase in the Van Deempter equation, and explain all terms appearing in it. (3)

iii. Explain the role of an internal standard in chromatography (3)